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COATINGS

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GLAZE COATINGS BASED ON PYROXENE GLASS OBTAINED WITH THE ADDITION OF GROUP-II OXIDE PAIRS

N. F. Shcherbina[1, 2] and T. V. Kochetkova[1, 3]

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The results of investigations of the effect of group-II element oxides introduced simultaneously into glaze batch on the properties of pyroxene glass are presented. It is shown that introducing two oxides of group-II elements simultaneously improves the adhesion properties of glass and lowers its melting temperature and CLTE. The glazes obtained can be used to coat decorative ceramic articles.

Key words: aegirite, aegirite-diopside, pyroxene glass, glaze, properties.

The production of glass coatings for ceramics requires the development of new materials possessing a certain complex of properties making it possible to obtain articles of high quality. A shortage of most of the materials commonly used in the production of such articles makes it necessary to study the possibility of using natural mineral raw materials for these purposes.

The byproducts of combined processing of apatite-nepheline ores are nepheline, pyroxene, titanium-magnetite and other concentrates. Among the iron-containing raw materials pyroxene concentrates are of great interest for the synthesis of glaze glass. Their advantage lies in the fact that they contain, aside from iron compounds, alkali and alkali-earth metal compounds. The particularities of the crystalline structure of pyroxene raw materials create the prerequisites for the synthesis of glaze glasses on par with conventional raw materials. The mutual substitution of ions occurs in pyroxenes and, in addition, continual and complete substitution exists between a few minerals belonging to this group and partial substitution between many. Since a large number of compounds of different elements can participate in isomorphic exchange with each one having a corresponding effect on the properties of the crystalline phase, the prerequisites for the synthesis of glaze coatings with a wide range of compositions, properties and color are created. The use of pyroxene concentrates in the compositions of glazes makes it possible to obtain colored transparent and crystallized glasses with different colors (from light-gray to virtually black) [1, 2].

It has been established that the introduction of the oxides of group-II elements (ZnO, CdO, BaO, SrO, MgO, CaO) into the composition of pyroxene glass lowers the melting temperature and viscosity of the glass (compositions with calcium and magnesium oxides are exceptions). Zinc and magnesium oxides lower the linear thermal expansion temperature coefficient (CLTE) [1].

The present work is a continuation of research on glaze glasses based on pyroxene raw material and focuses on the effect of the combined introduction of the oxides of group-II elements on the properties of glazes based on it. In the present work two oxides of group-two elements were introduced into the optimal composition of the experimental systems and their effect on the properties of pyroxene glasses was determined. The optimal compositions of pyroxene glasses are presented in Table 1.

The initial pyroxene-based glasses have a matte light-brown color. The main crystalline phase is ulvospinel, which is uniformly distributed in a glassy phase. The present studies were performed on the systems aegirite-nepheline – quartz – boric acid – 2RO and aegirite-diopside – nepheline – quartz – boric acid – 2RO. The pairs ZnO–BaO and ZnO–MgO were introduced as group-II oxides in different ratios. The oxides were introduced into the batch above 100%. The chemical composition of the initial components and the batch composition are presented in Table 2 and 3.

[1] I. V. Tananaev Institute of the Chemistry and Technology of Rare Elements and Minerals, Kola Scientific Center (IKhTRÉMS KNTs RAN), Apatity, Russia.
[2] E-mail: sherb_nf@chemy.kolasc.net.ru.
[3] E-mail: Koche_TV@chemy.kolasc.net.ru.

TABLE 1. Optimal Composition of Pyroxene Glasses

Material	Oxide content, wt.%										
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	P_2O_5	B_2O_3
Aegirite based glass	51.03	11.06	1.68	7.52	0.70	1.44	0.61	2.43	7.73	0.01	15.79
Aegirite-diopside based glass	48.93	11.36	2.90	5.41	0.99	4.00	1.40	2.76	2.76	0.25	15.80

TABLE 2. Chemical Composition of the Components of the Glaze Batch

Oxides	Oxide content in the batch components, wt.%				
	Aegirite-diopside concentrate	Aegirite concentrate	Quartz concentrate, Ena deposit	Boric acid	Nepheline concentrate
SiO_2	43.69	51.19	97.00	–	44.28
Al_2O_3	3.46	2.26	1.62	–	29.48
TiO_2	6.95	2.65	0.007	–	2.79
Fe_2O_3	18.42	26.09	1.38	–	0.59
FeO	3.04	1.98	–	–	0.41
CaO	12.07	2.94	–	–	1.74
MgO	4.38	1.72	–	–	0.25
K_2O	1.27	0.13	–	–	7.15
Na_2O	5.32	11.01	–	–	13.28
P_2O_5	0.62	–	–	–	0.03
B_2O_3	–	–	–	56.32	–
MnO	0.58	0.30	–	–	0.10
V_2O_5	0.20	–	–	–	–
F	–	–	–	–	–
Other	–	–	–	42.70	–

TABLE 3. Batch Composition

Composition No.	Component content in batch, wt.%							
	Components			Quartz, Ena deposit	Boric acid	ZnO	BaO	MgO
	Aegirite-diopside	aegirite	nepheline					
1	25	–	30	20	25	3	2	–
2	25	–	30	20	25	5	2	–
3	–	25	30	20	25	3	2	–
4	–	25	30	20	25	5	2	–
5	25	–	30	20	25	3	–	2
6	25	–	30	20	25	5	–	2
7	–	25	30	20	25	3	–	2
8	–	25	30	20	25	5	–	2

To prepare the batch the initial components were mixed in the required amounts and placed into corundum crucibles in a silit furnace for melting. The frits were melted at temperature 1350°C and soaked at the final temperature for 1 h. The ready frit was poured into cold water to cool, dried and comminuted in a porcelain mill to complete passage through a 0.063 mm sieve.

Samples in the form of 0.5 mm pellets were prepared to study the properties of the synthesized glazes. The pellets were place on a substrate comprised of low-melting clay and fired in a silit furnace in the temperature interval 950 – 1100°C every 50°C. The temperature in the furnace was raised at the rate 180 K/h; the soaking time at the final temperature was 2.5 h. The following properties of the samples obtained were determined: adhesion (spreadability), microhardness, CLTE, melting temperature, flow temperature, fusibility, phase composition and color. The chemical composition of the frit with the addition of two group-II oxides and the CLTE were calculated by A. A. Appen's method [3]. It was found that the experimental glazes do not spread adequately in the temperature interval 950 – 1050°C. Satisfactory spreading is observed for all compositions at 1100°C. The results obtained are presented in Table 4.

Data analysis shows that introducing two group-II oxides together improves the adhesion properties of glasses by decreasing the spreadability of glass to 200 – 220 mm compared with previously studied glasses (140 – 150 mm). Increasing the content of zinc oxide from 3 to 5 %[4] together with 2% barium oxide into aegirite-diopside glass increases the microhardness from 6570 to 6780 MPa. In similar compositions of aegirite glass the microhardness decreases from 6910 to 6740 MPa. Substituting 2% MgO for 2% BaO in aegirite-diopside glass decreases the microhardness from 7440 to 6460 MPa, while in aegirite glass it increases from 6520 to 6920 MPa.

The investigations showed that introducing two group-II oxides together lowers the melting temperature in pyroxene glasses with respect to similar glasses with only one oxide added.

The simultaneous introduction of ZnO and MgO into aegirite-diopside compositions makes it possible to lower the CLTE of the glass from 62.71×10^{-7} to $59.47 \times 10^{-7}\ K^{-1}$, while in aegirite glasses the CLTE remains practically unchanged and equal to $64.9 \times 10^{-7} – 64.5 \times 10^{-7}\ K^{-1}$. Introducing zinc and barium oxides as pairs into glass compositions decreases the CLTE in aegirite-diopside compositions from 63.04×10^{-7} to $62.7 \times 10^{-7}\ K^{-1}$ and has no effect on the CLTE in aegirite glasses $66.9 \times 10^{-7} – 67.1 \times 10^{-7}\ K^{-1}$ com-

[4] Here and below, the content by weight, wt.%, unless otherwise stipulated.

TABLE 4. Properties of Synthesized Glazes

Composition No.	Glaze properties						
	Spreadability, mm	Microhardness, MPa	CLTE, 10^{-7} K^{-1}	Melting temperature, °C	Flow temperature, °C	Fusibility, °C	Glaze color
1	210	6570	63.04	830	878.6	0.64	Brown, lustrous
2	220	6780	62.73	830	869.8	0.68	Brown, lustrous
3	200	6910	67.12	810	878.6	0.66	Gray-brown, lustrous
4	200	6740	66.89	825	861.0	0.69	Gray-cherry, lustrous
5	220	7740	59.47	860	900.6	0.61	Gray-cherry, lustrous
6	220	6460	62.71	860	857.8	0.71	Dark-cherry, lustrous
7	210	6560	65.45	830	887.4	0.64	Lilac, lustrous
8	200	6920	64.99	830	874.2	0.67	Dark-lilac, lustrous

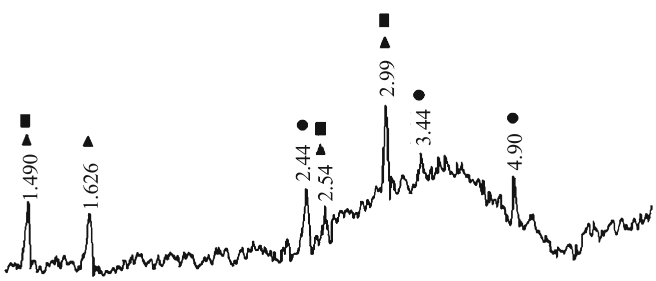

Fig. 1. X-ray diffraction pattern of glaze based on aegirite-diopside with the addition of 5% ZnO and 2% MgO: ■) ulvospinel Fe_2TiO_4; ▲) franklinite $ZnFe_2O_4$; ●) pseudobrookite Fe_2TiO_3.

pared with systems where only one group-II oxide was introduced.

The coefficient of crystallinity K_{cr}, which makes it possible to determine the structural state of glaze glasses and predict the form and quality of the glaze coating, was calculated as follows:

$$K_{cr} = \frac{CaO + MgO + SiO_2 + TiO_2 + Fe_2O_3 + FeO}{Al_2O_3 + Na_2O + K_2O + B_2O_3 + ZnO + BaO} \geq 3.5.$$

The coefficient of crystallinity shows the ratio of the oxides (content by weight) in the composition of the most likely crystalline phases and oxides forming the glassy matrix [4]. For the experimental glasses it lies in the range 1.39 – 1.64. The data obtained show that the crystallization capacity the experimental glasses is low, which is confirmed by x-ray phase and microscopic analysis. The main phase in the aegirite and aegirite-diopside glasses with the addition of two group-II oxides is a glass phase. Small quantities of a crystalline phase in the form of ulvospinel, pseudobrookite and franklinite are present in the aegirite-diopside glasses when 5% ZnO and 2% MgO are added to the composition. The phase composition of the glaze is presented in Fig. 1. The crystals are nonuniformly distributed in the glassy phase. The introduction of 3% ZnO and 2% BaO into aegirite glasses also results in the appearance of a small quantity of ulvospinel. As these investigations have shown, the simultaneous introduction of two group-II oxides into aegirite glass makes the glass practically amorphous.

To determine the heat resistance and water permeability of glazes based on the glasses obtained, slip suspensions with density 1.43 – 1.53 g/cm^3 were prepared and deposited on the ceramic article by immersion. After drying the articles were fired and the heat resistance and water permeability of the glaze coating were determined. It was determined that the heat resistance of the glaze coating lies near 200°C and water permeability vanishes after 24 h.

In summary, the introduction of two group-II oxides at the same time into pyroxene compositions decreases the melting temperature of the glass, increases the spreadability and lowers the CLTE. The glazes obtained by adding ZnO, BaO and MgO simultaneously can be used for coating decorative ceramic articles.

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